PRJ, Vol. 4. (January 1992); P. 68–71, 5 FIGS, 2 TABLES.

## Short Note

# STUDY OF CORROSION DAMAGE TO CU/NI CHLORINATOR LINE BY SEA WATER

M.L. Mehta* and A.T. Hassan*

# دراسة حول تآكل خط أنابيب تزويد الكلور

م. ل. مهتا وعبد الفتاح حسن

تعرّض جزء من خط تزويد الكلور في بعض المنشآت إلى تحفر بسبب تأثير وسط محدث (ماء البحر). وقد أجريت الإختبارات للكشف عن الأضرار التي تعرض لها السطح كما تم تحليل مخلفات التآكل كيميائياً وذلك لتحديد أسباب العطب.

---

## BACKGROUND AND CASE HISTORY

The chlorinator line which failed was delivering sea water and hypochloride to the stilling tube of sea water lift pump 29/X–OIC to treat sea water continuously with 2 ppm of hypochloride to control microorganism. After every five to six hours, shock treatment of about 5 ppm of hypochloride for half an hour was also being given. This chlorinator line was 38 mm ($1\frac{1}{2}$ inch) in diameter with a wall thickness of 1.5 mm. Its material is reported to be 90–10 copper-nickel alloy. A flow velocity of 0.45 m/sec (1.5 ft/sec) was used. At times this line was shut down and thus flow was not always continuous.

Failure in the form of perforation/leak occurred at some distances from the outlet of the chlorinator line after it had been in operation for $1\frac{1}{2}$ years.

The objective of this study is:

(i) To investigate nature/type of corrosion damage and cause of perforation.

(ii) To determine chemical composition to check whether the material of chlorinator line is as per specification.

*Petroleum Research Centre, P.O. Box 6431, Tripoli, G.S.P.L.A.J.

## LABORATORY INVESTIGATIONS

(A) Visual observations

(B) Microscopic examination

(C) Analysis of corrosion product layer found on the alloy surface

(D) Chemical composition of tube material

### (A) Visual Observations

Failed section of the chlorinated tube in the as-received condition is shown in Fig. 1. It had been cut

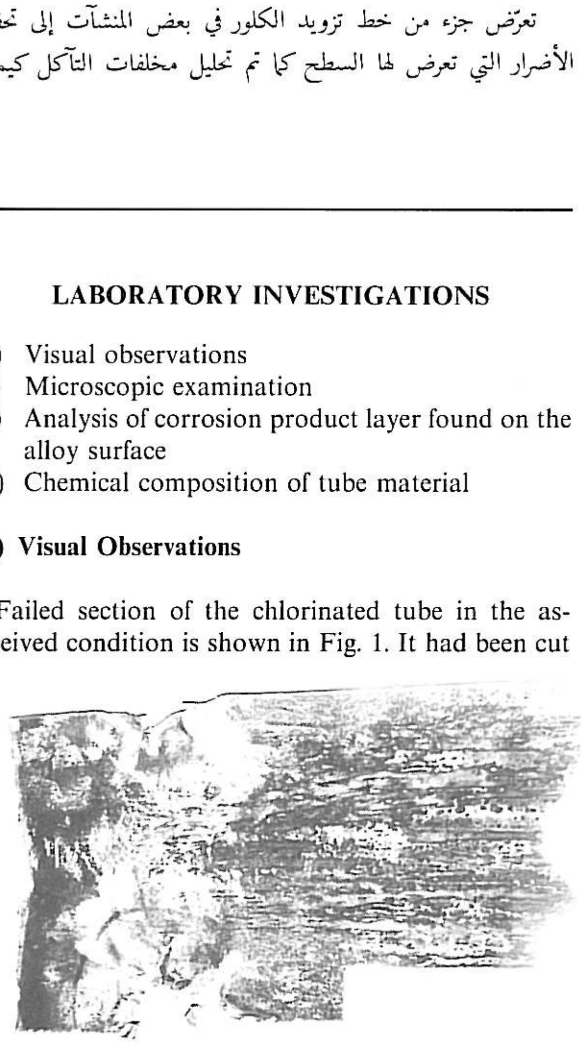

FIG. 1. As received failed section of chlorinator line showing extensive pitting, channels and perforation.

longitudinally and then flattened. The internal surface shows extensive pitting corrosion and formation of channels/grooves. Pits are shallow and degree of pitting is different in different regions. Colour of the surface film formed on the alloy substrate is mostly dark brown in colour and in some regions such as original substrate film is dark brown, spotty and not very adherent. The area surrounding the perforation is partly covered with the film and has finer pits but no channels (Fig. 1). Thickness was measured at different locations and are marked in Fig. 1. In the region surrounding the leak thickness had been reduced to 0.5 mm compared with original thickness of 1.5 mm indicating considerable corrosion in this localized area.

### (B) Metallographic Examination

The morphology of localized attack tend towards horse-shoe morphology (Fig. 2 a,b). Initially pits are formed as seen in Fig. 3a and then these pits grow to emerge into one another leading to the observed morphology. These horse-shoe attack propagate further leading to channel formation as illustrated in Fig. 3b. Within the horse-shoes cracked corrosion product layer was detected as in Fig. 4. In perforated/leaked region shallow horse shoe morphology of attack is observed (Fig. 5), but no channels/grooves were formed.

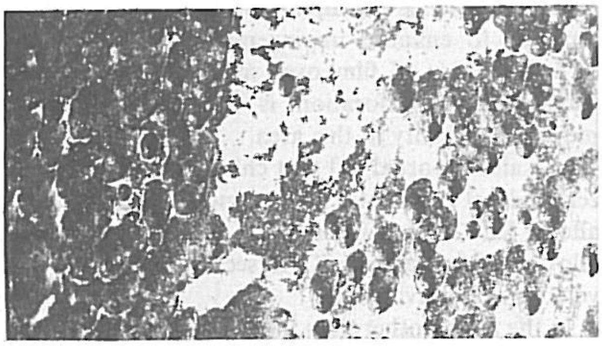

FIG. 2(a). Corrosion attack tending towards horse-shoe morphology. × 6.4.

FIG. 2(b). Corrosion attack tending towards horse-shoe morphology. × 16.

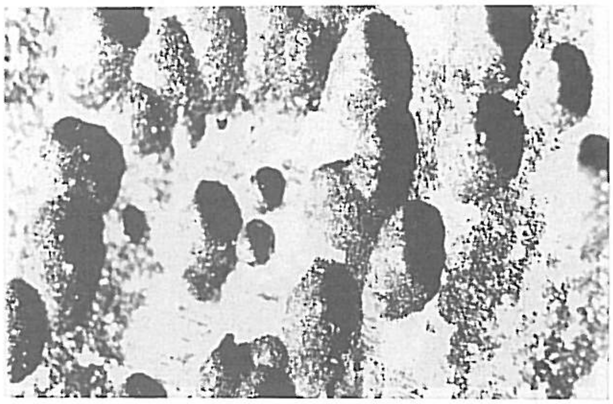

FIG. 3(a). Showing early stages of pit formations in original substrate and growth of pits into horse-shoe morphology and channel formation.

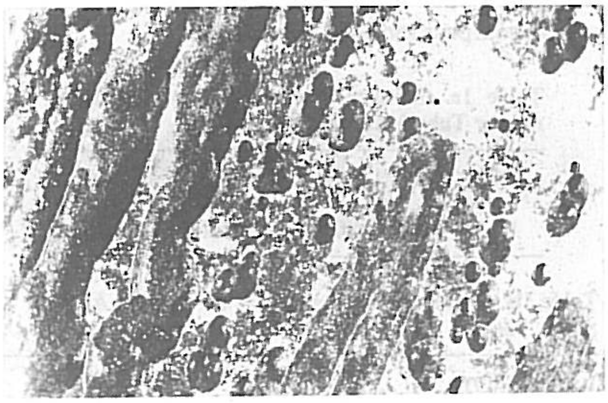

FIG. 3(b). Side-way growth of channels leading to wider channel. × 16.

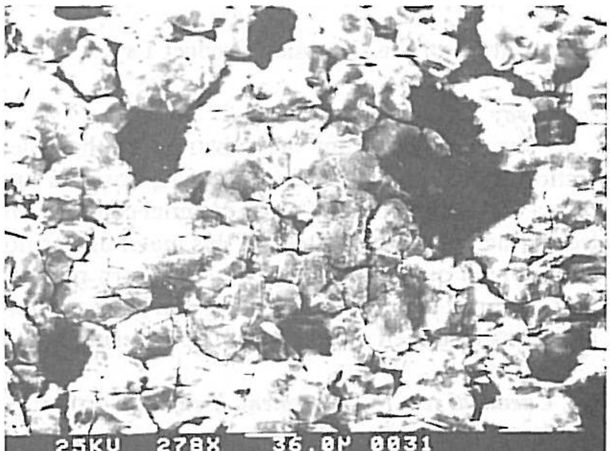


FIG. 4. Scanning electron micrograph showing cracked corrosion product within a horse-shoe.

### (C) Chemical Composition

The chemical composition of the material was determined using atomic absorption spectrometer and is given in Table 1a. It confirms the material to be 90-10 Cu/Ni alloy. As per standard designation for

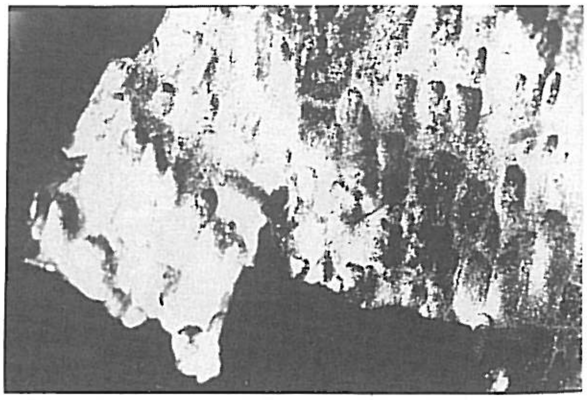

FIG. 5. Horse-shoe morphology of corrosion attack at the perforation site. × 6.4.

copper and copper alloys the composition in Table 1a corresponds to copper alloy number C 70600 whose composition is listed in Table 1b.

**Table 1a. Chemical Composition of the Chlorinator Tube Material (wt%)**

| Ni | Fe | Mn | Cr | Cu |
|---|---|---|---|---|
| 11.0 | 1.91 | 0.66 | 0.029 | balance |

**Table 1b. Chemical Composition of the Copper Alloy No. C 70600**

| Copper alloy No. | Cu | Pb | Fe | Zn | Ni | Mn |
|---|---|---|---|---|---|---|
| C 70600 | 86.5% | 0.05% | 1.0–1.8% | 1.0% | 9–11% | 1.0% |

## (D) Analysis of the Corrosion Product Layer

### (*a*) *X-ray diffraction analysis*

It was scrapped from the substrate of the failed section shown in Fig. 1. Since the film was thin and only a very small quantity of the material could be collected, the diffraction pattern of this material was not of very high quality. Analysis of the pattern revealed that scrapped material constituting corrosion product layer was identified to consist of coprous sulphide.

### (*b*) *Chemical test to supplement X-ray diffraction results*

Sodium azide test for the identification of sulphide in the corrosion product layer was carried out. Nitrogen gas bubble were evolved upon immersing corroded pieces of Cu/Ni alloy in the sodium azide-iodine reagent indicating the presence of sulphide in the product.

Upon standing the test solution along with corroded pieces the solution became nearly colourless as the reaction, $NaN_3 + I_2S \xrightarrow{S} 2NaI_3 + 3N_2$ approaches to completion as iodine converts to NaI. This observation confirms that sulphide is present in the corrosion product scrapped from the substrate. In the above reaction sulphide acts as a catalyst.

## DISCUSSION

The results of the present investigations reveal formation of sulphide surface film on the alloy substrate and suggest the presence of sulphide in the sea water flowing through the chlorinator line. When cuprous sulphide forms as the principal corrosion product layer on the copper alloy surface as in the present case it lacks passivity [1]. It is reported [2] that even the presence of sulphide as low as 0.007 ppm in the sea-water causes localized sulphide induced attack. Increasing level of sulphide accelrates the attack. It is well established [3] that the conventional Cu/Ni alloys are known to perform adhersely in polluted sea water, pollutant being sulphide.

Flow velocity in the chlorinator line is 0.45 m/sec (1.5 ft/sec) and is much lower than minimum flow velocity required to result in erosion-corosion. Perforation in the chlorinator line has been caused by localized impingement attack. It is difficult to establish the cause of the localized enhancement of flow required.

One of the main causes of localized impingement attack in a straight tube as in the present case is some sort of partial internal logdement causing local turbulence. Presence of sulphide in sea water has been reported to enhance impingement attack. The observed absence of film over most of the area surrounding the perforation is indicative of higher prevailing velocity in this area.

It is also reported [4] that chlorine dosing above a certain level accelerates impingement attack in Cu/Ni alloys. Safe level is 0.2 mg/l for 90-10 copper-nickel alloy at a flow velocity of 9 m/sec. Data at lower flow velocity is not available.

In the region other than the impingement area bulk flow velocity has been smaller as indicated by the morphology of attack. Ellison and Wen [5] have proposed three fundamentally different mechanisms for the interaction between fluid flow and corrosion, namely convective mass transfer controlled corrosion, phase transport controlled corrosion, and erosion-corrosion. The horse-shoe morphology is indicative of mass transfer controlled corrosion [6]. The reaction rate is controlled by connective mass transfer. Any flow disturbances will cause shallow pits or grooves in areas with locally high mass transfer.

## CONCLUSIONS

(i) Formation of cuprous sulphide film on alloy substrate is detected and indicates the presence of sulphide in the sea water.

(ii) Corrosion damage to chlorinator tube is attributed to accelerated attack induced by the presence of sulphide in the sea water.

## ACKNOWLEDGEMENT

The authors would like to thank the Petroleum Reseach Centre Management for their support and encouragement.

## REFERENCES

[1] Encyclopedia of Industrial Chemical analysis, 1973, Vol. 18, p. 393.
[2] Gilbert, P.T., 1982, Materials Performance, Vo. 21, p. 47.
[3] Syrett, B.C., 1981, Materials Performance, Vol. 20, p. 50.
[4] Francis, R., 1982, Materials Peformance, Vol. 21, p. 44.
[5] Ellison, B.T. and Wen, C.J., 1981, Am. Inst. Chem. Eng. Symp. Ser., Vol. 77, p. 161.
[6] Sybergr, T., 1987, Br. Corros. J., No. 2, p. 83.